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(54) Olefin resin-metal bonded structure and process for its preparation

(57) An olefin resin layer is bonded to a metal substrate through a primer layer comprising (a) a polar group-containing ethylenically unsaturated monomer-modified olefin resin having a specific polar group concentration and a specific degree of crystallization and (B) a coating film-forming base resin, the primer layer has a multi-layer distribution structure comprising the base resin (B) distributed predominantly in the portion contiguous with the surface of the metal substrate and the modified resin (A) distributed predominantly in the portion contiguous to the olefin resin layer and having defined concentration gradients of the two components (A) and (B) with respect to the thickness direction. With this primer layer, the bonding strength between the metal substrate and the olefin resin and the corrosion resistance of the metal substrate can be remarkably improved and also the processability of the olefin resin-metal bonded structure can be remarkably improved.

of from 0.2/99.8 to 40/60 and said primer layer having a multi-layer distribution structure having such concentration gradients of both the components (A) and (B) with respect to the thickness direction that the base resin (B) is distributed predominantly in the portion contiguous to the surface of the metal substrate and the modified olefin resin (A) is distributed predominantly in the portion contiguous to the surface of the olefin resin layer, wherein when said primer layer is divided into three sub-layers with respect to the thickness direction, the distribution ratio defined by the following formula:

$$D_x = \frac{W_x \times 10000}{W \times C_A}$$

wherein D_x stands for the distribution ratio, W stands for the weight (mg/dm^2) of the primer layer per unit surface area, C_A stands for the average content (% by weight) of the modified olefin resin in the primer layer, and W_x stands for the weight (mg/dm^2) of the modified olefin resin in each sub-layer per unit area, is at least 50 % in the sub-layer contiguous to the olefin resin layer and the distribution ratio is not higher than 10 % in the sub-layer contiguous to the surface of the metal substrate.

In accordance with another fundamental aspect of the present invention, there is provided a process for the preparation of olefin resin-metal bonded structures comprising applying an undercoat paint onto a metal substrate and fusion-bonding an olefin resin layer to the metal substrate through a layer of the undercoat paint, wherein said undercoat paint comprises (A) a polar group-containing ethylenically unsaturated monomer-modified olefin resin containing polar groups at a concentration of 0.01 to 200 milliequivalents per 100 g of the polymer and having a degree of crystallization of at least 50 % and (B) a coating film-forming base resin at an (A)/(B) weight ratio of from 0.2/99.8 to 40/60 in a mixed solvent containing at least 70 % by weight of a solvent component having a solubility parameter of from 8.5 to 9.5 in which the difference between the boiling point of a solvent having a highest boiling point and the boiling point of a solvent having a lowest boiling point is at least 20°C.

The present invention will now be described in detail.

Metals and alloys such as iron, steel, copper, aluminum, zinc, stainless steel, bronze, cupronickel, duralmin and die casting alloys may be used as the metal substrate in the present invention. Further, the metal substrate may be composed of steel plated with zinc, tin, chromium or the like or steel treated with phosphoric acid or electrolytically treated with chromic acid. The shape of the metal substrate is not particularly critical. For example, the metal substrate may be in the form of a metal foil, a rolled thin plate, a panel, a sheet, a rod, a beam, other formed material, a wire, a twisted wire, a crown shell, a cap, other vessel, a construction material or a vehicle construction. The present invention may preferably be applied to an untreated steel plate (so-called black plate), a steel plate having the surface treated with phosphoric acid or chromic acid or electrolytically treated with chromic acid and a steel plate having the surface electrolytically plated or fusion-plated with tin, zinc or the like. When the present invention is applied to these metal substrates, the bondability to an olefin resin can be effectively enhanced while improving the corrosion resistance of the metal substrates per se remarkably. In order to attain an anti-corrosive effect, the surface of the metal substrate may be coated in advance with a known primer such as an epoxy-amino resin, a phenol-epoxy resin, an epoxy-urea resin, a phenol-epoxy-vinyl resin, an epoxy-vinyl resin or the like.

One of the important features of the present invention is that when an olefin resin is bonded to a metal substrate through a primer layer, by using a combination of a specific modified olefin resin (A) and a coating film-forming base resin (B) as the primer layer, in the primer layer there is manifested a multi-layer distribution structure having such concentration gradients of the two components with respect to the thickness direction that the base resin (B) is distributed predominantly in the portion contiguous to the surface of the metal substrate and the modified olefin resin (A) is distributed predominantly in the portion contiguous to the surface of the olefin resin layer.

In the present invention, it is important that the modified olefin resin (A) used in the present invention should contain polar groups such as described hereinafter at a concentration of 0.01 to 200 milliequivalents per 100 g of the polymer, preferably 0.1 to 70 milliequivalents per 100 g of the polymer and should have a degree of crystallization of at least 50 %, preferably at least 70 %. Namely, in order to manifest the above-mentioned multi-layer distribution structure in the primer layer and improve the mechanical bonding strength between the polyolefin layer and the primer layer, the bonding strength resistant to water or hot water and the processability of the bonded area, it is important that the foregoing requirements should be satisfied in the modified olefin resin (A).

The degree of crystallization in the modified olefin resin has significant influences on the property of forming in the primer layer the above-mentioned multi-layer distribution structure having specific concentration gradients with respect to the thickness direction. Incidentally, the degree of crystallization referred to in the instant specification and appended claims is one determined according to the X-ray diffraction method described in the Journal of Polymer Science, 18, pp. 17-26 (1955) (S. L. Aggarwal and G. D. Tilley). When the degree of crystallization is lower than 50 % in the modified resin (A), it is possible to disperse the modified olefin resin (A) into the coating film-forming base resin (B) but it is very difficult to

portion contiguous to the olefin resin layer.

The concentration of polar groups in the modified olefin resin (A) has significant influences on the compatibility or affinity of the modified olefin resin (A) with the coating film-forming base resin (B) and the polyolefin layer and also on the property of forming in the primer layer the multi-layer distribution structure having concentration gradients with respect to the thickness direction. When the polar group concentration in the modified olefin resin (A) is below the above-mentioned range, the compatibility of the modified olefin resin (A) with the base resin (B) is lowered and as a result, even if the modified olefin resin (A) is distributed predominantly in the top face portion of the primary layer, bonding having a satisfactory strength can hardly be formed between the polyolefin layer and the primer layer.

If the polar group concentration in the modified olefin resin (A) exceeds the above-mentioned olefin resin (A) with the olefin resin layer, bonding having a satisfactory strength can hardly be formed between the polyolefin layer and the primer layer, or because of too high compatibility or affinity of the modified olefin resin (A) with the base resin (B), it is difficult to form a multi-layer distribution structure in which the modified olefin resin (A) is distributed predominantly in the top face portion of the primer layer.

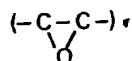
In contrast, when a modified olefin resin having a degree of crystallization of at least 50 % and containing polar groups at a concentration of 0.01 to 200 milliequivalents per 100 g of the polymer is selected and used as the modified olefin resin (A) according to the present invention, it is possible to manifest prominently in the primer layer a novel multi-layer distribution structure in which the modified olefin resin (A) is distributed predominantly in the upper portion and the base resin (B) is distributed predominantly in the lower portion, and it is possible to bond the olefin resin layer to the metal substrate with a highest strength through the specific modified olefin resin-base resin distribution structure in the primer layer. Further, although incorporation of a modified olefin resin into the primer layer tends to reduce the corrosion resistance of the metal substrate, if the above-mentioned multi-layer distribution structure is manifested in the primer layer according to the present invention, it is possible to impart to the metal substrate a high corrosion resistance comparable to the corrosion resistance attainable by a primer layer free of a modified olefin resin.

In the present invention, any of products formed by incorporating known polar group-containing ethylenically unsaturated monomers into main or side chains of olefin resins by known treatments such as graft copolymerization, block copolymerization, random polymerization and terminal treatment can be used as the modified olefin resin in the present invention, so far as the foregoing requirements are satisfied.

As the polar group-containing ethylenically unsaturated monomer, there can be used monomers having a carbonyl group



derived from a carboxylic acid, a carboxylic acid salt, a carboxylic anhydride, a carboxylic acid ester, a carboxylic acid amide or imide, an aldehyde or a ketone, monomers having a cyano group ($\text{-C}\equiv\text{N}$), monomers having a hydroxyl group, monomers having an ether group and monomers having an oxirane ring



These monomers may be used singly or in the form of a mixture of two or more of them. Suitable examples of monomers are as follows:

(1) Carbonyl group-containing monomers:

(1-A) Ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, crotonic acid, itaconic acid, citraconic acid and 5-norbornene-2,3-dicarboxylic acid.

(1-B) Ethylenically unsaturated carboxylic anhydrides such as maleic anhydride, citraconic anhydride, 5-norbornene-2,3-dicarboxylic anhydride and tetrahydrophthalic anhydride.

(1-C) Ethylenically unsaturated esters such as ethyl acrylate, methyl methacrylate, 2-ethylhexyl acrylate monoethyl maleate, diethyl maleate, vinyl acetate and vinyl propionate.

(1-D) Ethylenically unsaturated amides and imides such as acrylamide, methacrylamide and maleimide.

(1-E) Ethylenically unsaturated aldehydes and ketones such as acrolein, methacrolein, vinylmethyl ketone and vinylbutyl ketone.

(2) Cyano group-containing monomers such as acrylonitrile and methacrylonitrile.

(3) Hydroxyl group-containing monomers such as propyl γ -hydroxymethacrylate and ethyl β -hydroxyacrylate.

(4) Ether group-containing monomers such as vinylmethyl ether, vinylethyl ether and allylethyl ether.

(5) Oxirane ring-containing monomers such as glycidyl acrylate, glycidyl methacrylate and glycidylvinyl ether.

In the present invention, among the foregoing monomers, ethylenically unsaturated carboxylic acids and ethylenically unsaturated carboxylic anhydrides are especially preferred. These monomers are used

Such polar group-containing monomer is bonded to the main or side chain of an olefin resin so that the polar group concentration is in the above-mentioned range and the degree of crystallization of the resulting modified olefin resin is at least 50 %.

As the olefin, there can be mentioned, for example, ethylene, propylene, butene-1, pentene-1 and 4-methylpentene-1. These olefins are used singly or in the form of a mixture of two or more of them.

In order to modify an olefin resin so that the foregoing requirements are satisfied, for example, in case of the grafting treatment, it is necessary to select an olefin resin having a degree of crystallization of at least 50 % as the starting olefin resin and conduct the grafting treatment under such conditions that the degree of crystallization of the olefin resin is not reduced below 50 %. For this reason, high density polyethylene or isotactic polypropylene or a highly crystalline ethylene-propylene copolymer is preferably employed as the trunk polymer. Further, under such mild grafting conditions as will not cause any substantial reduction of the degree of crystallization, medium density polyethylene and low density polyethylene having a degree of crystallization higher than 50 % can also be used.

The grafting treatment can be conducted under known conditions so far as the above requirements are satisfied. For example, when a trunk polymer composed of an olefin resin is contacted with a polar group-containing ethylenically unsaturated monomer in the presence of a radical initiator or under application of radical initiating means, a modified olefin resin can easily be obtained. The trunk polymer may be contacted with the monomer in a homogeneous solution system, a solid-liquid or solid-gas heterogeneous system or a homogeneous melt system. As the radical initiator, there can be mentioned, for example, organic peroxides such as dicumyl peroxide, t-butyl hydroperoxide, dibenzoyl peroxide and dilauroyl peroxide and azonitriles such as azobisisobutyronitrile and azobisisopropionitrile. These initiators are used in known catalytic amounts. As the radical initiating means, there can be mentioned, for example, ionizing radiations such as X-rays, γ -rays and electron rays, ultraviolet rays, combinations of ultraviolet rays with sensitizers, and mechanical radical initiating means such as kneading (mastication) and ultrasonic vibration.

In case of reaction of the homogeneous solution system, the olefin resin, monomer and initiator are dissolved in an aromatic solvent such as toluene, xylene or tetralin, and the grafting reaction is carried out. The resulting modified olefin is recovered as a precipitate. In case of reaction of the heterogeneous system, a powder of the olefin resin is contacted with the monomer or a dilution of the monomer under ionizing radiations to effect grafting. In case of reaction of the homogeneous melt system, a blend of the olefin resin and monomer optionally with the initiator is melt-extruded by an extruder or kneader to form a modified olefin resin. In each case, the resulting modified olefin resin may be subjected to a purifying treatment such as washing or extraction so as to remove the unreacted monomer, the homopolymer or the residual initiator. Further, when the resulting modified olefin resin is recrystallized from an aromatic solvent such as mentioned above and the crystallization conditions are appropriately controlled, the particle size can be adjusted.

A modified olefin resin (A) that is used in the present invention can easily be prepared in the foregoing manner.

Any of known base resins for formation of anti-corrosive primer layers can be used as the coating film-forming base resin (B) in the present invention. In general, in order to form the above-mentioned multi-layer distribution structure in the primer layer and increase the bondability of the primer layer to the metal substrate, it is preferred to use a coating film-forming base resin (B) having a density higher by at least 0.1 than the density of the modified olefin resin (A), generally a density of 1.2 to 1.3, and containing functional groups selected from the group consisting of hydroxyl groups and carbonyl groups at a concentration of at least 1 milliequivalent per gram of the polymer, especially 3 to 20 milliequivalents per gram of the polymer.

When a base resin having a density higher by at least 0.1 than the density of the modified olefin resin (A) is used, it becomes much easier to manifest the specific multi-layer distribution structure having concentration gradients specified in the present invention in the primer layer. Further, if the concentration of functional groups such as hydroxyl or carbonyl groups in the base resin is at least 1 milliequivalent per gram of the polymer, the adhesion of the primer layer to the metal substrate and the corrosion resistance can be further improved.

In the base resin to be used for forming a primer layer in the present invention, hydroxyl groups may be included in the main or side chain of the polymer in the form of an alcoholic hydroxyl group, a phenolic hydroxyl group or a mixture thereof, and carbonyl groups may be introduced into the main or side chain of the polymer in the form of a carboxylic acid, carboxylic acid salt, carboxylic acid ester, carboxylic acid amide, ketone, imide, urea or urethane.

A resin meeting the foregoing requirements is selected among thermosetting and thermoplastic resin vehicles customarily used in the art of paints. For example, there can be used thermosetting resins such as phenol-formaldehyde resins, urea-formaldehyde resins, melamine-formaldehyde resins, xylene-formaldehyde resins, epoxy resins, alkyd resins, polyester resins, thermosetting acrylic resins, urethane resins and mixtures thereof, and thermoplastic resins such as acrylic resins, vinyl chloride-vinyl acetate copolymers, vinyl chloride-vinyl acetate-maleic acid copolymers, vinyl butyral resins, other vinyl resins, styrene-butadiene-acrylic acid ester copolymers, polyamide resins and petroleum resins, so far as they

So-called thermosetting resins are preferably employed as base resins for formation of primers in the present invention, and among them, phenolic resin-epoxy resin paints, urea resin-epoxy resin paints, melamine resin-epoxy resin paints and phenolic resin-vinyl resin paints are especially preferred.

In forming a coating composition for preparing a primer layer, the modified olefin resin (A) is combined with the coating film-forming base resin (B) at an (A)/(B) weight ratio of from 0.2/99.8 to 40/60. In the present invention, since in the primer layer the base resin (B) is distributed predominantly in the portion contiguous to the metal substrate and the modified olefin resin (A) is distributed predominantly in the portion contiguous to the olefin resin layer bonded to the metal substrate through the primer layer, even if the content of the modified olefin resin (A) is as low as 0.2 % by weight, the bonding force between the primer layer and the olefin resin layer can be increased, and even if the content of the base resin (B) is as low as 60 % by weight, the adhesion between the primer layer and the metal substrate can be enhanced.

The amount of the primer layer coated on the metal surface, namely the weight of non-volatile resin solids per unit surface area of the metal substrate, is preferably 10 to 500 mg/dm², especially 30 to 100 mg/dm². If the amount coated of the primer layer is within this preferred range, a good combination of a high corrosion resistance and a high adhesion can be attained. It is particularly preferred that the amount coated of the modified olefin resin (A) be 0.01 to 100 mg/dm², especially 0.1 to 10 mg/dm², and the amount coated of the base resin (B) be 1 to 500 mg/dm², especially 10 to 100 mg/dm².

A liquid coating composition comprising the modified olefin resin (A) and the base resin (B) at the above-mentioned weight ratio in a mixed solvent described hereinafter is prepared, this composition is applied to the surface of the metal substrate to be bonded to the olefin resin, and the mixed solvent is evaporated to manifest the above-mentioned novel multi-layer distribution structure in the resulting primer layer.

In order to effectively manifest the multi-layer distribution structure in the primer layer, it is important that the mixed solvent should contain at least 70 % by weight of a solvent component having a solubility parameter (Sp value) of 8.5 to 9.5 and the difference between the boiling point of a solvent (S₁) having a highest boiling point in the mixed solvent and the boiling point of a solvent (S₂) having a lowest boiling point in the mixed solvent should be at least 20°C., preferably at least 25°C.

When a solvent having a solubility parameter (Sp value) included within the above range is used in an amount of at least 70 % by weight based on the total mixed solvent, the base resin (B) can be completely dissolved in the mixed solvent and the modified olefin resin (A) is dispersed or suspended in the form of fine particles having a so-called emulsion particle size, for example, 2 to 50 μ, especially 5 to 20 μ. If the so prepared paint is coated and baked, the above-mentioned multi-layer distribution structure can be stably formed. When a solvent having a solubility parameter (Sp value) included in the above range is not contained in the mixed solvent or its content is lower than 70 % by weight, it is ordinarily difficult to form a paint having the above-mentioned dispersion state and being capable of forming a multi-layer distribution structure.

When a single solvent is used or when the difference of the boiling point is smaller than 20°C. if a plurality of solvents are used, it is difficult to form a primer layer having the above-mentioned multi-layer distribution structure, and the processability of the primer-coated metal substrate or the polyolefin-metal bonded structure is not satisfactory. In contrast, when the modified olefin resin (A) and the base resin (B) are dissolved in the above-mentioned specific mixed solvent and the resulting paint is coated and dried, as will be apparent from Examples given hereinafter, there is formed a multi-layer structure in which the modified olefin resin is distributed predominantly in the surface portion of the resulting coating. The reason has not been completely elucidated, but it is believed that under conditions of drying or baking the coated paint, the temperature of the coating or the solvent composition is changed with a certain gradient while the solvents are evaporated and this change will promote formation of the multi-layer distribution structure.

The solvent (S₁) having a higher boiling point is used in an amount of 10 to 70 % by weight, especially 20 to 60 % by weight, based on the total solvents, and the solvent (S₂) having a lower boiling point is used in an amount of 10 to 70 % by weight, especially 20 to 60 % weight, based on the total solvents. Suitable combinations of solvents satisfying the foregoing requirements are selected from ketones such as acetone, methylethyl ketone, methylisobutyl ketone, cyclohexanone and isophorone, alcohols such as diacetone alcohol, n-butanol, methylcellosolve and butylcellosolve and aromatic hydrocarbons such as toluene, xylene and decalin.

Examples of suitable combinations of solvents are methylisobutyl ketone/methylethyl ketone, methylisobutyl ketone/diacetone alcohol/xylene, and n-butanol/xylene/ cyclohexanone/isophorone.

A coating composition for formation of the primer layer is prepared, for example, by dissolving the base resin (B) in one or more of the foregoing organic solvents to form a solution and adding the modified olefin resin (A) in the form of a solution in, for example, hot xylene or in decalin to the base resin solution to form a homogeneous composition. In general, it is preferred that the resin concentration in the so formed liquid coating composition be 10 to 50 % by weight.

When a primer layer is formed on the surface of the metal substrate, the surface of the metal substrate may be degreased and washed according to known means if desired, and the above-mentioned liquid coating composition is applied to the surface of the metal substrate according to known coating means.

deposition coating.

The liquid coating composition applied to the metal substrate is then dried or baked under heating. In general, it is preferred that the heating be carried out at a temperature higher than the melting point of the modified olefin resin (A), especially 150 to 200°C. By this heat treatment, the base resin (B) is distributed predominantly in the portion contiguous to the metal substrate and the modified olefin resin (A) is distributed in the surface portion of the primer layer, whereby a multi-layer distribution structure is formed. The reason has not been completely elucidated. It is however believed that in the combination of the modified olefin resin (A) and base resin (B) having the above-mentioned specific properties, under drying conditions a tendency to cause phase separation between the two resins is brought about and the modified olefin resin (A) having a lower specific gravity is caused to rise in the surface portion, and that this tendency to cause phase separation is promoted by evaporation of the solvents. In the case where the base resin is a thermosetting resin, curing of the base resin is caused by the heat treatment, and it is believed that formation of the multi-layer distribution structure will be promoted also by curing of the base resin.

Any of heating devices may be used for this heat treatment so far as the temperature condition is within the above-mentioned range. For example, heating furnaces customarily used for baking of coatings, such as a hot air furnace, an infrared heating furnace, a high frequency induction heating furnace and the like, can optionally be used in the present invention.

From the viewpoints of the operation facility and the productivity, it is most preferred that the modified olefin resin (A) and base resin (B) constituting the primer layer be applied in the form of a liquid coating composition comprising both the resins. A primer layer having the above-mentioned multi-layer distribution structure can also be formed according to the following method.

A solution containing the base resin (B) alone is coated on the cleaned surface of the metal substrate, a solution or fine dispersion of the modified olefin resin (A) is coated on the coating of the base resin, and the resulting composite coating heated at a temperature higher than the melting point of the modified olefin resin (A). In this case, in order to dissolve both the resins in each other in the interface between the two resin coatings and form a multi-layer structure primer layer having a high peel strength, it is important that a solution or dispersion of the modified olefin resin (B) and the composite coating should be heated at a temperature higher than the melting point of the modified olefin resin (A). For example, when a coating of the modified olefin resin is formed on a baked coating of the base resin, a polyolefin-metal bonded structure having a high bonding strength cannot be obtained at all. The reason is considered to be that peeling is readily caused between the base resin layer and the modified olefin resin layer. Namely, when this latter coating method is adopted, it is important that sufficient mingling of both the resins should take place in the interface between the base resin layer and the modified olefin resin layer or in areas adjacent to the interface. In this coating method, other conditions such as amounts coated of the respective resins, coating means and heat treatment means may be the same as in the first-mentioned method.

In the present invention, according to any of the above methods, there is formed a primer layer having a multi-layer distribution structure having such concentration gradients with respect to the thickness direction that the base resin (B) is distributed predominantly in the portion contiguous to the surface of the metal substrate and the modified olefin resin (A) is distributed predominantly in the portion contiguous to the surface to be bonded to an olefin resin.

In the present invention, a so-called double-coat primer layer may be formed by coating a known primer coating composition free from the modified olefin resin (A) on the metal substrate and then applying a liquid coating composition containing the modified olefin resin (A) and base resin (B) to this primer coating.

The fact that the primer layer formed according to the present invention has the above-mentioned multi-layer distribution structure can be confirmed by dividing the primer layer in the thickness direction into the following three sub-layers, namely a topmost sub-layer (L_s) nearest to the metal substrate, an intermediate sub-layer (L_m) and a lowermost sub-layer (L_b), and determining distribution ratios (contents, %) of the modified olefin resin in the respective sub-layers.

More specifically, a heat-treated primer coating is caused to fall in contact with steel wool attached to a rotation shaft and a layer having a predetermined thickness (about 1 μ) is peeled off by abrasion. The iron component is removed from the powder of the peeled coating by using a magnet and the residual powder is subjected to infrared absorption spectrum analysis according to the KBr tablet method. An absorption not overlapping the characteristic absorption of the base resin (B), in general, an absorption owing to the stretching vibration of the methylene group at 2920 cm^{-1} , is chosen as the characteristic absorption of the modified olefin resin, and the concentration of the modified olefin resin (A) is determined based on a calibration curve prepared in advance.

In the bonded structure of the present invention, the primer layer is characterized in that (1) the distribution ratio of the modified olefin resin (A) is at least 50 % (all of "%" and "parts" are by weight unless otherwise indicated), especially at least 70 %, in the topmost sub-layer (L_s), and that (2) the distribution ratio of the modified olefin resin (A) is not higher than 10 %, especially not higher than 5 %, in the lowermost sub-layer (L_b).

The distribution ratio referred to in the instant specification and appended claims is defined by the following formula:

$$D_X = \frac{W_X \times 10000}{W \times C_A}$$

wherein D_X stands for the distribution ratio, W stands for the weight (mg/dm^2) of the primer layer per unit surface area, C_A stands for the average content (% by weight) of the modified olefin resin in the primer layer, and W_X stands for the weight (mg/cm^2) of the modified resin per unit area in each sub-layer [the uppermost sub-layer (L_s), the intermediate sub-layer (L_m) or the lowermost sub-layer (L_b)].

From experimental results shown in Examples given hereinafter, it will readily be understood that by formation of the above-mentioned multi-layer distribution structure in the primer layer, the peel strength of the resulting bonded structure is remarkably improved and also the corrosion resistance is improved.

As the olefin resin to be applied to the above-mentioned primer layer in the present invention, there can be used, for example, polyolefins such as low density polyethylene, medium density polyethylene, high density polyethylene, isotactic polypropylene, ethylene/butene-1 copolymers, polybutene-1, ethylene/hexene copolymers, ethylene/propylene copolymers and ethylene/propylene/conjugated diene terpolymers, and olefin copolymers and modified polyolefins composed mainly of an olefin and containing a small amount of an ethylenically unsaturated monomer other than an olefin. As such olefin copolymer and modified polyolefin, there can be mentioned, for example, ethylene/vinyl acetate copolymers (EVA), saponified ethylene/vinyl acetate copolymers (EVAL), ethylene/acrylic acid copolymers, ethylene/methyl methacrylate copolymers, polyethylenes modified with unsaturated carboxylic acids such as maleic acid, acrylic acid, methacrylic acid and esters thereof, polypropylenes modified with unsaturated carboxylic acids such as maleic acid, acrylic acid and esters thereof, ionomers and chlorosulfonated polyethylene.

These olefin resins may be used singly or in the form of a mixture of two or more of them. One or more of elastomers such as ethylene/propylene rubber (EPR), ethylene/propylene/diene rubber (EPDM), polyisobutylene (PIB), butyl rubber (IIR), polybutadiene (PB), natural rubber (NR), stereospecific polyisoprene, nitrile rubber (NBR) (styrene/butadiene copolymer, styrene/butadiene block copolymer, styrene/isoprene copolymer or styrene/isoprene copolymer) and polychloroprene (CR) may be incorporated in amount of 1 to 60 % by weight into polyethylene, polypropylene or EVA, whereby elastic properties necessary for packings or sealants can be improved.

Various additives may be incorporated into the polyolefin according to recipes known in the art. For example, there may be incorporated antioxidants or stabilizers of the phenol type, organic sulfur type, organic nitrogen type or organic phosphorus type, lubricants such as metal soaps or other fatty acid derivatives, fillers such as calcium carbonate, white carbon, titanium white, magnesium carbonate, magnesium silicate, carbon black and clays, and coloring agents.

A cross-linking agent, a foaming agent or a mixture thereof may be incorporated into the olefin resin that is used in the present invention, and a cross-linked, foamed or cross-lined and foamed olefin resin layer may be formed. For example, when it is desired to form a coating of an olefin resin excellent in heat resistance, durability and mechanical properties such as elasticity on the metal substrate, it is recommended to incorporate a cross-linking agent in the olefin resin. When it is desired to form a coating excellent in the cushioning property necessary for a packing or sealant, it is preferred to incorporate a foaming agent, optionally with a cross-linking agent, into the olefin resin.

As such cross-linking agent and foaming agent, there can be used, for example, cross-linking agents decomposing at temperatures approximating to the processing temperature (softening point) of the resin used, such as organic peroxides, e.g., dicumyl peroxide, di-*t*-butyl peroxide, cumyl hydroperoxide and 2,5-dimethyl-2,5-di(*t*-butylperoxy)-hexane-3, and foaming agents decomposing at temperatures approximating to the processing temperature of the resin used, such as 2,2'-azobisisobutyronitrile, azodicarbonamides and 4,4-hydroxybenzenesulfonylhydrazide. The cross-linking agent is used in an amount of 0.1 to 5 % by weight based on the resin and the foaming agent is used in an amount of 0.2 to 10 % by weight based on the resin.

The olefin resin layer is heat-bonded to the metal substrate through the above-mentioned primer layer at a temperature higher by at least 10°C . than a higher temperature between the melting point of the modified olefin resin (A) and the melting point of the olefin resin, generally at 120 to 300°C ., preferably at 150 to 230°C . The olefin resin is applied in the form of a film, sheet, powder or other molded article to the primer layer formed on the metal substrate, and the olefin resin is heated at the above-mentioned temperature to fusion-bond the olefin resin to the primer and then, the assembly is cooled to obtain a bonded structure. Heating of the olefin resin is accomplished by various means, for example, (a) passing the assembly through a heated furnace, (b) heating the assembly by the heat transferred from a heated press or roll, (c) heating the metal substrate in advance or in situ by high frequency induction heating or the like or roll, and (d) heating the assembly by infrared rays,

As another method for bonding the olefin resin to the metal substrate through the primer layer, there can be mentioned a method comprising extruding a melt of the olefin resin at the above-mentioned temperature on the primer layer formed on the metal substrate to fusion-bond the olefin resin to the metal substrate through the primer layer. In this method, the molten olefin resin may be applied in the form of a continuous molded article such as a tape, film, sheet, tube or sheath onto the metal substrate according to a so-called extrusion coating technique. Further, there may be adopted a method in which the molten olefin resin is extruded in the form of a mass on the metal substrate and fusion-bonded to the metal substrate while the molten olefin resin being cooled and molded into a desirable shape by a roll, press or stamper. The former extrusion coating method is advantageous when a continuous coating of the olefin resin formed on the metal substrate, and the latter method is advantageous when a layer of the olefin resin is formed in a specific portion of the metal substrate. Fusion bonding of the olefin resin to the metal substrate can be completed for a very short time of the microsecond or millisecond order if desired.

When the olefin resin applied to the metal substrate is cross-linked, foamed or cross-linked and foamed, after fusion-bonding of the olefin layer to the primer layer on the metal substrate the olefin resin layer is heated at a temperature higher than the decomposition temperature of the foaming agent or cross-linking agent.

When the metal substrate is a thin structure such as a metal foil, thin sheet, tube or thin vessel, the olefin resin layer may be applied to only one surface of the metal substrate or both the surfaces of the metal substrate. Further, a sandwiched bonded structure may be formed by fusion-bonding both the surfaces of the olefin resin layer to metal substrates such as foils or sheets.

In the bonded structure of the present invention, by heat-bonding the olefin resin layer to the metal substrate through the primer layer interposed therebetween, which has the above-mentioned specific multi-layer distribution structure, the peel strength between the olefin resin layer and the metal substrate can be remarkably improved. In a bonded structure formed by fusion-bonding the olefin resin layer to the metal substrate directly without an intermediate primer layer, corrosion of the metal substrate is readily caused in the interface between the metal substrate and resin layer, and extreme corrosion of the metal substrate advances from the uncoated portion or edge portion in this bonded structure unless the entire surface of the metal substrate is completely covered with the olefin resin, and this advance of corrosion accelerates peeling of the olefin resin layer from the metal substrate. Such troubles owing to corrosion can be effectively eliminated in the present invention by forming the above-mentioned specific primer layer in advance on the metal substrate.

As will be apparent from the foregoing illustration, the present invention is very advantageous for production of crown closures, bottle caps, can lids and other vessel closures including a packing or sealant of an olefin resin. Further, by virtue of the above-mentioned desirable combination of high peel resistance and high corrosion resistance, the bonded structure of the present invention can be advantageously used for production of various lined vessels such as cans, tanks, chemical reaction vessels and flexible packages, construction materials and vehicle construction materials such as wall plates and roofing materials, and various ordinary utensils such as laminate tables, decorating materials, heat insulating materials, coated wires, coated cables and the like.

The present invention will now be described in detail by reference to the following Examples that by no means limit the scope of the invention.

Example 1

A mixture of 1.0 mole of p-cresol, 1.2 moles of formaldehyde and 0.2 mole of ammonia was reacted on a water bath to form an ammonia-resol resin. Then, 40 parts by weight of the so prepared resin and 60 parts by weight of a bisphenol A type epoxy resin (Epikote[®] 1007 manufactured by Shell Chemical) were dissolved in an organic solvent (mixed solvent of equal amounts of methylisobutyl ketone and methylethyl ketone) to form a base resin solution. A polyolefin indicated in Table 1 was dissolved in heated xylene at a concentration of 10 % by weight. This solution was added to the base resin solution under sufficient agitation so that the amount of the polyolefin added to the base resin was as indicated in Table 1: Thus, a primer coating composition having a total solid content of about 30 % by weight was prepared.

The primer coating composition was roll-coated on a surface-treated steel plate having a thickness of 0.2 mm (Hi-Top[®] manufactured by Toyo Seikan) in such an amount that the thickness after curing and drying would be 6 μ , and the applied composition was heated at 200°C. for 10 minutes to form a coated steel plate.

The modified polyolefin resin used in this Example was prepared according to the known method in the following manner.

A stainless steel pressure vessel equipped with a dropping funnel, a thermometer and agitation blades was used as the reaction vessel. In case of samples E-1 to E-6, polyethylene having a degree of crystallization of 93.1 % and a melt index of 2 was used as the starting polyolefin, and in case of samples E-7 to E-10, polyethylene having a degree of crystallization of 90.2 % and a melt index of 0.2 was used as the starting polyolefin. In case of sample E-11, polyethylene having a degree of crystallization of 67.5 % and a melt index of 12 was used as the starting polyolefin. In case of sample P-1, polypropylene having a degree of crystallization of 75.1 % and a melt index of 5 was used as the starting polyolefin. The starting

polyolefin and p-xylene were charged in the reaction vessel, the inside atmosphere was replaced by nitrogen and the mixture was heated to form a xylene solution containing 10 % by weight of the polyolefin. Under agitation, a p-xylene solution of maleic anhydride and a p-xylene solution of dicumyl peroxide were added dropwise to the so formed polyolefin solution. The reaction conditions and the amount added of maleic anhydride were appropriately adjusted so that the degree of modification shown in Table 1 could be attained. The amount added of dicumyl peroxide was 0.7 g per 100 g of the starting polyolefin. The reaction temperature was selected from the range of 125 to 165°C. and the maleic anhydride solution was added over a period of 4 to 10 hours. The amount added of maleic anhydride was the calculated amount necessary for attaining the intended degree of modification (polar group concentration). After completion of the reaction, the reaction mixture was cooled and the resulting modified polyolefin resin was recovered by filtration and washed with acetone. The degree of crystallization of the recovered modified polyolefin was determined according to the X-ray diffraction method and the degree of modification with maleic anhydride was determined according to the elementary analysis method. Obtained results are shown in Table 1.

The corrosion resistance of the above-mentioned coated steel plate was evaluated based on the degree of rusting after 10 days' outdoor exposure, and the processability was evaluated based on the degree of formation of damages at the test of bending to 2T. The coating layer (primer layer) was divided into three thin sub-layers having a thickness of about 2 μ (topmost sub-layer L_s , intermediate sub-layer L_m and lowermost sub-layer L_b) according to the surface polishing method. The amount of the modified polyethylene in each sub-layer was determined according to the infrared absorption spectrum method and the distribution ratio (%) was calculated. Obtained results are shown in Table 1.

A sheet composed of low density polyethylene (having a melt index of 2 and a density of 0.920) and having a thickness of about 0.5 mm was heat-bonded to the coated steel plate under a pressure of 5 Kg/cm² at 180°C. for 3 minutes by using a hot press, and the assembly was quickly cooled to form a metal substrate/coating composition/polyethylene bonded structure. The peel strength between the polyethylene and the metal substrate was determined at a peeling speed of 50 mm/min, a temperature of 20°C. and a peeling angle of 180° by using an Instron type universal tensile tester to obtain results shown in Table 1.

Table 1

Sample No.*	Degree (%) of Crystallization	Polyolefin Degree (meq/100g) of Modifi- cation	Amount Added (% by weight)	Distribution Ratio (%) of Polyolefin		Sub- Layer L _B	Peel St- rength (g/cm) of Bonded Structure	Properties of Coated Steel Plate	
				Sub- Layer L _S	Sub- Layer L _M			Corrosion Resistance	Process- ability
Comparison 1			0	0	0	0	0	0	Δ
Comparison 2			20	98.5	1.0	0.5	0	Δ	X
E-1	93.1	0	20	94.0	5.8	0.2	850	0	0
E-2	92.5	0.01	20	91.2	8.0	0.8	1050	0	0
E-3	87.1	0.58	20	86.5	12.1	1.4	2720	0	0
E-4	74.9	30.5	20	80.1	14.7	5.2	1460	0	0
E-5	69.2	72.2	20	57.5	32.7	9.8	550	0	Δ
E-6	60.7	206	20	37.4	34.5	28.1	120	X	X
(Comparison 3)	48.9	253	20						
E-7	87.1	0.58	1.0	99.3	0.6	0.1	930	0	0
E-8	87.1	0.58	5.0	95.5	4.2	0.3	1000	0	0
E-9	87.1	0.58	30	75.5	21.0	3.5	1120	0	0
E-10	87.1	0.58	50	54.8	27.2	18.0	400	X	X
(Comparison 4)									
E-11	65.8	10.2	20	59.2	33.4	7.4	1050	0	0
P-1	60.9	50.6	20	79.7	14.3	6.0	2120	0	0

Note

Comparison 1: sample free of a modified polyolefin

Comparison 2: sample in which unmodified high sensity polyethylene was added

E: sample in which maleic anhydride-modified polyethylene was added

5 P: sample in which maleic anhydride-modified polypropylene was added

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From the results shown in Table 1, it will readily be understood that in the bonded structure according to the present invention, the modified polyolefin is distributed predominantly in the surface portion of the primer layer. However, if the degree of crystallization or degree of modification is outside the range specified in the present invention as in comparison 3, the predominant distribution of the modified

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10 polyolefin cannot be attained in the surface portion and properties of the primer coating are degraded.

Further, when the amount added of the modified polyolefin is too large as in comparison 4, no smooth and lustrous coating can be obtained, and the bonding strength is reduced and peeling is caused in the interface between the coating layer and the metal substrate.

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15 *Example 2*

To 80 parts by weight of the same base resin composition as used in Example 1 was further added 20 parts by weight of a low-molecular-weight vinyl chloride/vinyl acetate copolymer (VYHH® manufactured by Union Carbide), and the so obtained base resin composition was dissolved in an organic solvent

(comprising 35 parts of MIBK, 35 parts of MEK, 25 parts of xylene and 5 parts of isophorone) to form a

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20 base resin solution. Then, the same maleic anhydride-modified polyethylene solution in 120°C. xylene as used for formation of sample E-8 in Example 1 was added in an amount of 5 % by weight as solids into

the above base resin solution to form a primer coating composition having a solid content of 30 % by weight. In the same manner as described in Example 1, a metal/coating layer/polyethylene bonded struc-

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25 ture was prepared by using the so prepared primer coating composition. For comparison, a bonded structure was prepared in the same manner as above except that oxidized polyethylene (having a molecu-

lar weight of 5000, a density of 0.96 and a saponification value of 19.2 mg ROH/g) was used instead of the

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30 maleic anhydride-modified polyethylene. With respect to each of these two bonded structures, 10 lots were prepared. Namely, such steps as preparation of the primer coating composition, formation of the

coating on the steel plate and laminatio of polyethylene were conducted 10 times, and in each lot, 20

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35 samples were prepared. Accordingly, 200 samples were prepared with respect to each bonded structure.

With respect to two kinds of the bonded structures, the peel strength of the polyethylene layer was

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measured and deviations among the lots were calculated. As a result, in case of the bonded structure of the present invention, it was found that the average peel strength was 1020 g/cm and the standard deviation was 0.052, but in case of comparative bonded structure, it was found that the average peel strength

was 900 g/cm and the standard deviation was 14.3. Accordingly, it was confirmed that bonded structures

having excellent properties can be obtained very stably according to the present invention.

Example 3

In the same manner as described in Example 1, a primer composition having a total solid content of

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40 30 % by weight was prepared. Namely, a base resin composition comprising 50 parts by weight of an acrylic resin prepared from 2 moles of glycidyl methacrylate and 4 moles of 2-ethylhexyl acrylate and 50

parts by weight of an epoxy resin (Epikote 1009) was dissolved in a mixed solvent (comprising 35 parts of MIBK, 35 parts of MEK and 30 parts of xylene) to form a base resin solution, and a primer coating com-

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45 position containing maleic anhydride-modified polyethylene (same as used for formation of sample E-3 in Example 1) at a concentration of 15 % by weight based on the solids in the base resin solution was

prepared in the same manner as described in Example 1. Then, in the same manner as described in

Example 1, the primer coating composition was coated on one surface of a tinplate sheet and then baked.

On the opposite surface, an epoxy-amino paint layer, a print layer and an overcoat layer (epoxy ester type resin) were formed in succession to form a both surface-coated sheet.

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50 From this coated sheet, crown shells were prepared by a crown-forming press so that the printed surface was located outside. Polyethylene liners were formed on these crown shells. More specifically,

polyethylene (having a melt index of 7 and a density of 0.92) was melt-extruded from an extruder pro-

vided with a nozzle 5 mm in diameter and having a diameter of 40 mm and the molten extrudate was cut

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55 at the top end portion of the nozzle by a cutting blade so that about 300 mg of the melt was charged inside each crown shell. Immediately, punching was conducted by a cooled punch to form crown closures (hav-

ing a size of kind 5 specified by JIS S-9017 inner diameter = 26.6 mm). Bottles filled with carbonated drink

(inner pressure being 3 Kg/cm² at 20°C) were corked with these crown closures. These bottles were stored

at a temperature of 50°C. and a relative humidity of 100 % for 3 months. Such troubles as leakage of gas

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60 (reduction of the inner pressure) and rusting were hardly caused. Thus, it was confirmed that these crown closures had high practical utility.

CLAIMS

1. A bonded structure comprising a metal substrate and an olefin resin layer

containing ethylenically unsaturated monomer-modified olefin resin containing polar groups at a concentration of 0.01 to 200 milliequivalents per 100 g of the polymer and having a degree of crystallization of at least 50 % and (B) a coating film-forming base resin at an (A)/(B) weight ratio of from 0.2/99.8 to 40/60 and said primer layer having a multi-layer distribution structure having such concentration gradients of both the components (A) and (B) with respect to the thickness direction that the base resin (B) is distributed predominantly in the portion contiguous to the surface of the metal substrate and the modified olefin resin (A) is distributed predominantly in the portion contiguous to the surface of the olefin resin layer, wherein when said primer layer is divided into three sub-layers with respect to the thickness direction the distribution ratio defined by the following formula:

$$D_X = \frac{W_X \times 10000}{W \times C_A}$$

wherein D_X stands for the distribution ratio, W stands for the weight (mg/dm^2) of the primer layer per unit surface area, C_A stands for the average content (% by weight) of the modified olefin resin in the primer layer, and W_X stands for the weight (mg/dm^2) of the modified olefin resin in each sub-layer per unit area, is at least 50 % in the sub-layer (L_s) contiguous to the olefin resin layer and is not higher than 10 % in the sub-layer (L_s) contiguous to the surface of the metal substrate.

2. A bonded structure according to claim 1 wherein the modified olefin resin is an olefin resin grafted with an ethylenically unsaturated carboxylic acid or ethylenically unsaturated carboxylic anhydride.

3. A bonded structure according to claim 1 or 2 wherein the distribution ratio in the sub-layer (L_s) is at least 70 % and the distribution ratio in the sub-layer (L_s) is not higher than 5 %.

4. A bonded structure according to claim 1, 2 or 3 wherein the base resin (B) has a density higher by 0.1 g/cc than the density of the modified olefin resin (A) and contains functional groups selected from hydroxyl and carbonyl groups at a concentration of at least 1 milliequivalent per gram of the polymer.

5. A bonded structure according to any one of the preceding claims wherein the base resin is selected from phenolic resin-epoxy resin paints, urea resin-epoxy resin paints, melamine resin-epoxy paints and phenolic resin-epoxy resin-vinyl resin paints.

6. A bonded structure according to any one of the preceding claims wherein the modified olefin resin (A) is applied to the metal substrate in an amount coated of 0.1 to 10 mg/dm^2 and the base resin (B) is applied to the metal substrate in an amount coated of 10 to 100 mg/dm^2 .

7. A bonded structure according to any one of the preceding claims wherein a modified polyethylene-free undercoat layer composed of a resin selected from phenol-epoxy resins, epoxy-amino resins, vinyl-phenolic resins, epoxy-vinyl resins and phenol-epoxy vinyl resins is provided in an amount of 10 to 200 mg/dm^2 between said primer layer and said metal substrate.

8. A bonded structure according to any one of the preceding claims which is in the form of a vessel closure.

9. A bonded structure according to claim 8 wherein the metal substrate is a crown shell or cap shell and the olefin resin layer is a packing.

10. A bonded structure according to claim 1 substantially as described in any one of the Examples.

11. A process for the preparation of a bonded structure as claimed in any one of the preceding claims, which process comprises applying an undercoat paint onto a metal substrate and fusion-bonding an olefin resin layer to the metal substrate through a layer of the undercoat paint, wherein said undercoat paint comprises the modified olefin resin (A) and the base resin (B) in an (A)/(B) weight ratio of from 0.2/99.8 to 40/60 in a mixed solvent containing at least 70 % by weight of a solvent component having a solubility parameter of from 8.5 to 9.5 in which the difference between the boiling point of the solvent having the highest boiling point and the boiling point of the solvent having the lowest boiling point is at least 20°C.

12. A process according to claim 11 substantially as described in any one of the Examples.

13. A bonded structure when prepared by a process as claimed in claim 11 or 12.

14. A vessel sealed with a vessel closure as claimed in claim 8 or 9.

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